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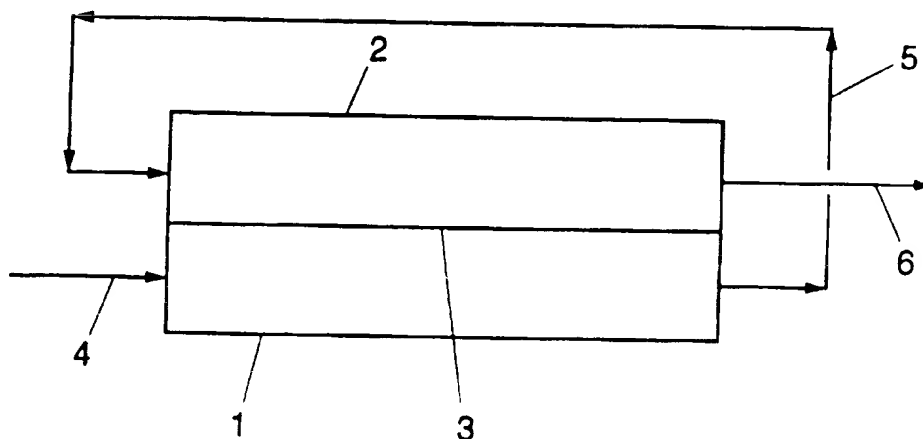
(57) Abstract

The invention relates to a method for carrying out two chemical reactions in a reactor system comprising at least two mutually separate reactor beds, of which the surfaces exposed to the reactants are catalytically active for the chemical reactions concerned, and at least one partition, wherein at least one first reactor bed is present, which is bounded by at least one partition, which bed is based on a continuous porous structure and which bed is fixedly connected to said partition, at least one second bed is present, which is based on a continuous porous structure and which bed is fixedly connected to said partition, and said second bed, with respect to the first bed, is disposed on the other side of said partition, so that a heat exchanging contact between said beds is present and the reaction heat of a first chemical reaction which is carried out in said first reactor bed is supplied or absorbed by carrying out a second chemical reaction in said second bed

Title: Method for carrying out a chemical reaction

The invention relates to a method for carrying out
endothermic and exothermic chemical reactions.

A great many chemical reactions are characterized by a
positive heat effect (exothermic reaction) or a negative
5   heat effect (endothermic reaction). To enable chemical
reactions to proceed in the desired manner, an efficient
supply or removal of the reaction heat is indispensable. In
some exothermic reactions, the thermodynamic equilibrium
shifts in an undesired direction if the temperature rises.
10   Examples are the synthesis of ammonia and methanol, the
oxidation of sulfur dioxide to sulfur trioxide in the
production of sulfuric acid, the reaction of sulfur dioxide
with hydrogen sulfide in the Claus process, the selective
oxidation of H_2S to elementary sulfur and the reaction of
15   carbon monoxide with hydrogen to methane. Since in the
course of these reactions thermal energy is released, the
temperature of the reaction mixture will rise and the
thermodynamic equilibrium will shift in an unfavorable
direction, unless the reaction heat released is removed fast
20   and efficiently from the reactor.

In endothermic reactions too, a shift of the
thermodynamic equilibrium in an undesired direction can
occur, now by the consumption of thermal energy. Examples
are methane-steam reforming and the dehydrogenation of
25   ethylbenzene to styrene. A problem may also arise in that as
a result of the consumption of energy by the reaction, the
temperature of the reaction mixture decreases unduly, so
that the desired reaction no longer proceeds.

Not only can a temperature change cause a shift of the
30   thermodynamic equilibrium in an unfavorable direction, it
can also adversely affect the selectivity of catalytic
reactions.

Examples of reactions where the temperature affects the
selectivity are the production of ethylene oxide from

ethylene (the undesired reaction is the formation of water and carbon dioxide), the selective oxidation of hydrogen sulfide to elementary sulfur (the undesired reaction is the formation of SO_2) and the Fischer Tropsch synthesis. In all
5   cases, a temperature rise occurs as a result of the release of the reaction heat. If this temperature rise is not prevented through a rapid removal of the reaction heat, the selectivity decreases greatly.

In most conventional catalytic reactors, use is made of
10 a fixed bed of catalyst particles. In such a catalyst bed, porous bodies of catalyst particles have been poured or piled.

In order to avoid an undesirably high pressure drop across such a catalyst bed, it is preferred to use bodies or
15 particles of dimensions of at least 0.3 mm. These minimum dimensions of the catalyst bodies are necessary to keep the pressure drop that occurs upon the passage of a stream of reactants through the catalyst bed, within technically acceptable limits. While the dimensions are limited at the
20 lower end of the range by the permissible pressure drop, the necessary activity of the catalyst imposes an upper limit on the dimensions of the catalytically active particles. The high activity required for a number of types of technical catalysts can mostly be achieved only with a surface of the
25 active phase of 25 to 500 m^2 per ml catalyst volume. Surfaces of such an order of magnitude are possible only with very small particles, for instance with particles of 0.05 μm. Since particles with such dimensions no longer allow a liquid or gas mixture to flow through them, the
30 primary, extremely small particles have to be formed into high-porous bodies with dimensions of at least about 0.3 mm which can possess a large catalytic surface. An important task in the production of technical catalysts is to combine the required high porosity with a sufficiently high
35 mechanical strength. The catalyst bodies cannot be allowed to disintegrate upon filling of the reactor and upon exposure to sudden temperature differences (thermal shock

Under the conditions of the thermal pretreatment and/or
catalytic reaction to be carried out, nearly all
catalytically active materials soon sinter to form large
conglomerates with a negligibly small active surface.
5   Therefore, the active component (finely divided) is
generally applied to a so-called support. This support
exhibits the necessary thermal stability and hardly sinters,
if at all, at high temperatures. Often used as supports are
silicon dioxide, aluminum oxide or activated carbon.
10   As appears from the above examples, there is a very
great need for a fast supply or removal of thermal energy in
catalytic reactors, but the total heat transfer coefficient
is mostly very low in a fixed catalyst bed. According to the
present state of the art, it is virtually impossible to
15   supply thermal energy to or remove it from a fixed catalyst
bed in an efficient manner. This is indeed evident from the
manner in which chemical reactions are carried out in fixed
catalyst beds.

It is possible that of an exothermic reaction only the
20   thermodynamic equilibrium shifts in adverse direction upon a
temperature rise, without the selectivity decreasing
unallowably. In that case, the reaction in a fixed catalyst
bed can be made to proceed adiabatically. After passage
through the reactor, the stream of reactants is cooled off
25   in a separate heat exchanger. Because the conversion of the
reactants is now thermodynamically limited by the
temperature rise in the reactor, the unconverted reactants
have to be reacted again upon cooling. The reaction product
can be separated and the reactants can be recycled through
30   the fixed catalyst bed. This occurs, for instance, in the
ammonia and methanol synthesis. If the reaction product
cannot be easily separated, downstream of the heat exchanger
a second fixed bed reactor with a heat exchanger must be
linked up. This is for instance the case in the oxidation of
35   sulfur dioxide to sulfur trioxide. Sometimes, to prevent
emission of harmful compounds, even a third reactor with
heat exchanger is necessary. If connecting a number of

reactors and heat exchangers in series is not properly possible and the separation of the reaction product is not either, the reaction product is sometimes recirculated through the catalyst bed. Per passage through the reactor,

5 so little of the reactants is added to the circulating reaction product that it is converted completely. Because the rise of the temperature must then be properly controlled, per passage through the reactor only very little can be converted. In cases where the reaction must be

10 carried out at a greatly increased pressure, the problems with the supply or removal of the reaction heat are extra large.

In the ammonia synthesis and the methanol synthesis, a catalyst bed is employed in which reactants are injected at

15 different points at a relatively low temperature.

Such an implementation of the method, whereby gas streams must be passed through high pressure reactors in a complicated manner, obviously also requires high investments.

20 In a number of technically important cases, it is desired in catalytic reactions to work with a high to very high spatial throughput rate, with a great pressure drop across the reactor being considered a less serious drawback In the conventional fixed bed reactors, a high pressure drop

25 with the corresponding high spatial throughput rate is not properly possible. If the pressure at the reactor inlet is increased, the catalyst may be blown (gaseous reactants) or washed (liquid reactants) out of the reactor. It is also possible that at a particular critical value of the pressure

30 at the reactor inlet "channeling" occurs. In that case, the catalyst particles in a particular part of the reactor are going to move. In that case, the reactants are found to flow virtually exclusively through the part of the catalyst bed that is in motion.

35 With the fixed bed reactors current at present, the catalyst bed clogs up. Therefore the reactor must be regularly opened and the cumulated layer of dust removed. It

would be favorable if a pulse of gas of high pressure could
be sent through the reactor in a direction opposite to that
of the stream of reactants. This pressure pulse would blow
the dust off the catalyst bed; thus, clogging could be
5   prevented without opening the reactor, which is technically
very attractive. With the fixed bed catalysts according to
the present state of the art, however, this is not possible;
along with the dust, the catalyst bodies would be blown out
of the catalyst bed.

10   It will be clear that a number of disadvantages can be
associated with the use of fixed bed reactors. In general,
it requires costly facilities, while recirculation and
separation of reaction products present in low concentration
require a great deal of energy. For that reason, in a number
15   of cases a whirling bed is employed. In a whirling bed the
transport of thermal energy is much easier, while the
problems with pressure drop and clogging do not occur. In a
whirling bed, however, the catalyst to be used must meet
very high standards regarding mechanical strength and wear
20   resistance, which is not at all possible with every
catalyst. Finally, the catalyst consumption in a whirling
bed is relatively high due to the unavoidable wear.
Accordingly, in many cases it will not be possible to use a
whirling bed.

25   There are cases where it is not possible to work either
with a whirling bed or with an adiabatic reactor. This
applies in particular to highly endothermic reactions and
reactions where the selectivity decreases unallowably upon
increase of the temperature. Examples are methane-steam
30   reforming and the selective oxidation of ethylene to
ethylene oxide. In a selective oxidation of ethylene, a very
large heat exchanging surface is employed by utilizing a
reactor with no less than 20,000 long tubes. In methane-
steam reforming it is attempted to optimize the heat supply
35   and to limit the pressure drop by adjusting the dimensions
and the shape of the catalyst bodies. In this last reaction

too, a large number of costly tubes have to be used in the reactor.

It has also been proposed to apply the catalyst exclusively to the wall of the reactor. An example of such a
5 system is described in the abstract of JP-A 6/111838. According to this publication, a reform catalyst has been provided in grooves of a plate, while in grooves of a second plate a combustion catalyst has been provided. These plates have been arranged against each other, so that through the
10 heat generated with the combustion the reforming can take place.

Also in carrying out the Fischer Tropsch reaction, in which from a mixture of hydrogen and carbon monoxide higher hydrocarbons are produced, a system has been employed, in
15 which a catalyst is provided on the wall of the reactor. This catalyst provided on the wall ensures a good heat transfer from the catalyst to the outside of the reactor. For providing the catalyst on the wall, *inter alia* the following method has been proposed. The catalyst is applied
20 as a Raney metal, an alloy of the active metal and aluminum. After being applied, the catalyst is activated by dissolving the aluminum with lye. The greater part of the reactor volume is empty, as a result of which the contact between the reactants and the catalytically active surface is slight
25 and the conversion per passage through the reactor is greatly limited. The reactants must therefore be frequently recirculated through the reactor.

In a number of technically important cases, the pressure drop upon passage of the reactants through the
30 catalyst bed must remain very low. This applies, for instance, to reactors in which flue gas of large plants is to be purified, as with the catalytic removal of nitrogen oxides from flue gas. Because a flue gas stream is generally very large, a substantial pressure drop requires a very
35 great deal of mechanical energy. The same applies to the purification of exhaust gases of automobiles. In this case too, a high pressure drop is unallowable

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Currently, the use of catalysts provided on a honeycomb is one of the few possibilities of achieving an acceptable pressure drop without unallowably reducing the contact with the catalyst. To that end, often ceramic honeycombs
5   (honeycombs, monoliths) are used, in which the catalytically active material has been provided.

A variant of the method in which the catalyst is provided exclusively on the wall, is the use of monoliths made up thin metal sheets. Such a reactor is manufactured,
10 for instance, by rolling up a combination of corrugated and flat thin metal sheets and subsequently welding them together. It is also possible to stack the flat sheets in a manner leading to a system with a large number of channels. On the wall of the thus-obtained channels the catalyst is
15 then provided.

As has been noted, the thermal conduction in a fixed catalyst bed is poor. This has been ascribed to the low thermal conductivity of the high-porous supports on which the catalytically active material has been provided.
20 Therefore Kovalanko, O.N. et al., Chemical Abstracts $\underline{97}$ (18) 151409u have proposed to improve the thermal conduction by increasing the conductivity of the catalyst bodies. They did this by using porous metal bodies as catalyst support. Now, it has already been described by Satterfield that the
25 thermal conductivity of a pile of porous bodies is determined not so much by the conductivity of the material of the bodies, as by the contacts between the bodies among themselves (C.N. Satterfield, "Mass Transfer in Heterogeneous Catalysis", MIT Press, Cambridge. MA.. USA
30 (1970), page 173). The inventors' own measurements have shown that the thermal conductivity of catalyst bodies indeed does not greatly affect the heat transport in a catalyst bed.

In WO-A 86/02016 a reactor is described. comprising a
35 reaction bed provided with a catalyst. which bed consists of sintered metal particles which are in good heat conducting communication with the reactor wall which wall is

externally provided with sintered metal particles for
removing reaction heat. Further, on the outside of the
reactor a phase transition occurs. Such a reactor system is
found to be able to realize a large heat dissipation, but
5   has the disadvantage that a good setting and/or control of
the reaction is not possible, or very difficult. This is
evident inter alia from the example in which the catalytic
combustion of a combustible gas with a heat of combustion of
35.530 kJ/m^3 is described. This would have to occur at a
10 temperature of 350°C. However, by the cooling of the reactor
with evaporating water (steam production) at 110°C, the
entire reactor is cooled to 110°C, so that the reaction will
not occur.

In US-A 4,101,287 a combined heat exchanger reactor is
15 described, consisting of a monolith, through a part of the
channels of which flow the reactants and through a part of
which flows the cooling agent. Here the same disadvantage as
in the system of WO-A 8602016 presents itself.

In EP-A 416710 a method is described, based on the use
20 of a catalytic reactor in which the reactor bed consists of
elementary particles of metal sintered to each other and to
one side of the reactor wall, while no sintered metal
particles are present on the other side of the reactor wall.
When in such a reactor the diameter of the reactor bed is
25 chosen in relation to the heat effects, which vary from one
reaction to another, but are known and, depending on the
reaction conditions, can be calculated, reactions of the
type referred to can be carried out optimally.

In carrying out chemical reactions, especially if they
30 are reactions which are carried out on a large scale, if a
strong heat effect is involved, or if high pressures are
required, problems accruing from the heat economy of the
reaction are encountered. It appears that in a number of
cases it is not easy to efficiently supply the necessary
35 heat or remove the heat produced. For instance in steam-
reforming natural gas or other hydrocarbons, the necessary
amount of heat is so large that complex systems with burner

and heating tubes are needed to supply the necessary heat.
This kind of problems also occurs with other reactions with
great thermal effects, such as the production of ammonia,
the preparation of ethylene oxide, the selective oxidation
5   of H_2S, and the like. Even in reactors according to the
above-mentioned EP-A 416710 or US-A 4,101,287, it is found
this can give rise to problems.

Presently, mixtures of hydrogen and carbon monoxide
(synthesis gas) are produced through reaction of methane
10   with steam, the so-called methane-steam reforming process.
If only hydrogen is desired, the carbon monoxide is allowed
to react with steam to form carbon dioxide and hydrogen. The
carbon dioxide formed is removed through dissolution under
pressure in aqueous solutions or regenerable solid sorbents
15   For this process, it is possible to use, besides
methane, other gaseous hydrocarbons or naphtha or other
hydrocarbons that can be readily brought into the gas phase.

To enable the highly endothermic reaction between
methane and steam to proceed, the necessary reaction heat
20   must be supplied to the reaction mixture at a high
temperature, for instance 850°C (allothermic process). In
general, the necessary heat is generated outside the
reaction mixture by combustion of, for instance, methane. In
order to transfer the thus generated thermal energy to the
25   reaction mixture, a partition with a sufficiently high
thermal conductivity must be used.

Through radiation the reaction heat generated in the
combustion reaction is transferred to the reaction mixture.
The reaction mixture is passed through tubes of a high-grade
30   alloy in which a suitable catalyst has been provided. The
tubes are exposed to the radiation of the burners.

To prevent oxidation of the tubes at the necessary high
temperatures, costly (nickel-containing) alloys must be used
for the reactor wall. To save energy, the methane-steam
35   reforming process is often carried out at elevated pressure
for instance at 30 bar, which imposes even more stringent
requirements of oxidation resistance

For the steam-reforming mentioned, it has previously been proposed to carry out a partial oxidation of the hydrocarbon prior to the reaction. The heat thereby produced is then stored in the gas and carried to the steam

5 reforming. Such a method, however, cannot be employed in all cases.

The object of the invention is to provide a suitable method for carrying out chemical reactions and in particular chemical reactions with a great thermal effect, whereby in a

10 simple manner the transport of the necessary or redundant heat is provided for.

The invention is based on the surprising insight that it is possible to optimally adjust the heat conduct of combined endothermic and exothermic reactions to each other

15 if use is made of a specific reactor system in which at least two reactor beds based on porous structures are in heat exchanging relation with each other.

The invention accordingly relates to a method for carrying out two chemical reactions in a reactor system

20 comprising at least two mutually separate reactor beds, of which the surfaces exposed to the reactants are catalytically active for the chemical reactions concerned, and at least one partition, wherein

- at least one first reactor bed is present, which is
25 bounded by at least one partition, which bed is based on a continuous porous structure and which bed is fixedly connected to said partition,

- at least one second bed is present, which is based on a continuous porous structure, and which bed is fixedly
30 connected to said partition, and

- said second bed, with respect to the first bed, is disposed on the other side of said partition, so that a heat exchanging contact between said beds is present and the reaction heat of a first chemical reaction which is
35 carried out in said first reactor bed is supplied or absorbed by carrying out a second chemical reaction in said second bed.

Over the above-described known systems, the invention has the advantage that during the process a greater stability is obtained, *inter alia* because of the self-regulating character of the system.

5   According to an embodiment of the method according to the invention, a reactor is used in which two or more first reactor beds and/or two or more second reactor beds are used which, through a corresponding number of partitions, are in heat exchanging relation with each other.

10   According to the invention, it is possible in a simple manner to efficiently transport the necessary heat to the desired place. According to a first variant of the method according to the invention, in the first reactor bed an endothermic reaction is carried out and in the second

15   reactor bed an exothermic reaction is carried out.

According to another variant of the invention, in the first reactor bed an exothermic reaction is carried out and in the second reactor bed an endothermic reaction is carried out.

20   According to yet another embodiment of the method according to the invention, a multi-stage reaction is carried out, wherein at least one stage of this reaction has a positive and at least one stage has a negative heat effect, and wherein said stages are carried out in said

25   first and second reactor bed.

An example of this last variant is formed by the above-mentioned steam reforming, preceded by partial oxidation. The heat necessary for the steam reforming is then supplied by the partial catalytic combustion of the hydrocarbon in

30   the first reactor bed, while the heat produced is supplied to the steam reforming via the common partition. The gases are thereupon supplied to the second reactor bed, where they are further converted.

Other suitable reactions that can be carried out

35   according to the invention are, for instance, the preparation of ethylene oxide, the selective oxidation of H_2S hydrogenation reactions, dehydrogenation reactions

such as the formation of styrene from ethylbenzene, the oxidation of methanol to formaldehyde, the conversion of methanol into synthesis gas, and the like. It is noted in this connection that the catalytic combustion of

5 hydrocarbons to form CO_2, water and heat, can also be regarded as a chemical reaction within the scope of this invention.

A suitable possibility for carrying out the method according to the invention, with the desired chemical

10 reaction being an endothermic reaction, is therefore the catalytic combustion of hydrocarbons, in particular natural gas, in the first reactor bed, while the endothermic reaction is carried out in the second reactor bed.

The catalytic combustion occurs in the presence of a

15 suitable combustion catalyst, for instance copper oxide or manganese oxide on a thermostable support. A very suitable catalyst is described, for instance, in EP-A 327,177. However, the art has a large number of other suitable combustion catalysts.

20 The chemical reactions that are carried out according to the invention take place under the most suitable conditions for the reactions chosen. With a view to a good heat exchange between the reactor beds, the temperatures in the two reactor beds will not differ greatly. In general,

25 the temperature difference will not be more than about 100°C, more particularly this difference will be less than 50°C. As a result, also the stability and the self-regulating character are improved.

Through a suitable choice of load and degree of

30 conversion in the two reactors, the temperatures in the two beds can be optimally adjusted to each other. In doing so, it is obviously possible to use all conventional variants in the manner of supplying reactants, recirculating a part of the reaction mixture, supplying or discharging reactants

35 and/or reaction products at different points in the reactor and the like.

The temperature employed in the reactors is dependent on the nature of the reactions. In general, an elevated temperature is employed, because then the advantages of the system are most pronounced. In general, the temperature will
5 be above 100°C, an upper limit being formed by the maximum temperature at which the material is still stable, or the temperature that can be achieved with a chemical reaction. However, temperatures in excess of 1250°C are generally not preferred because of the difficulties in achieving them and
10 the requirements that such temperatures impose on the materials of the reactors and the supply and discharge systems.

The pressures at which the various reactions are carried out, can be varied within wide limits, it being
15 noted that it is also possible to carry out the reactions at different pressures. Although this imposes more stringent requirements on the equipment, there is no fundamental problem.

In the present description, the term "partition" is
20 understood to refer to the physical separation between the space where the first reaction occurs, that is, the first reactor bed, and the space where the second reaction occurs, the second reactor bed. This can obviously be the outer wall of the catalyst bed, but it also encompasses, for instance,
25 a wall of channels of a monolith or the metal sheets of a rolled-up assembly.

The wall can consist of the conventional materials that are known for these purposes. These walls can consist of a single layer, but it is also possible to use more than one
30 layer, and it can specifically provide advantages if the surface to which the elementary bodies are to be fixedly connected, improves the bond with the elementary bodies. In this connection one can think, for instance, of the use of enamel coating in ceramic elementary bodies.
35 The continuous porous structure which is used in the reactor in accordance with the invention can be constructed in various ways, as will also appear from the further

explanation and the examples of suitable structures. In general, the continuous porous structure should meet the requirement that there is a heat exchanging contact between the partition and the structure, while further the porous
5   structure extends through the entire reactor bed.

This means that the porous structure is fixedly connected to at least one reactor wall, while the reactor bed consists of a structure which fills the entire reactor bed, at least, extends through the entire reactor bed, for
10 instance in the form of fixedly interconnected elementary particles, such as particles sintered together, or channels, arranged parallel, of a suitable sheet construction or of a monolith.

Accordingly, this does not encompass the system as
15 described in JP-A 6/111838, since no continuous porous structure is thereby obtained. In fact, the walls of each channel constitute a reaction wall, whereas according to the invention a porous structure is required.

With the invention, the degree of porosity of the
20 reactor bed can be varied within wide limits. This porosity, that is, the portion of the bed that allows gas or liquid to flow through, is generally between 20 and 95% by volume. The most suitable value depends on the nature of the reactor, the desired surface, the desired pressure drop and the
25 extent of heat transport in the bed.

The porosity can be distributed uniformly in the reactor bed, but it is also possible to provide a gradient in the porosity, for instance in the longitudinal direction viewed in the direction of flow of the reactants, or in the
30 transverse direction. It is also possible for this porosity not to be uniformly distributed through the reactor bed, for instance as is the case when a monolith is used.

The extent of heat transport is a relatively important factor in the reactor system according to the invention.
35 Obviously, the heat conductivity of the total system, that is, from the partition as far as into the beds, is partly determined by the heat conductivity of the material of the

catalyst support used and of the construction material of the reactor.

Preferably, the heat conductivity is not less than 10% of the heat conductivity of the material used in massive condition; preferably, this value is between 10 and 75%. In absolute terms, the heat conductivity is preferably between 0.2 and 300 W/m.K.

The heat conductivity is highly dependent on the heat conductivity of the elementary materials used. Al_2O_3 extrudate, for instance, has a conductivity of 0.32 W/m.K, while a sintered body of 316L has a value of 3-12 W/m.K. Powder of 316L, by contrast, has a value of 0.55, while massive material possesses 20 W/m.K. Massive copper has a heat conductivity of 398 W/m.K. All of these values relate to the condition at room temperature. At other temperatures, the absolute value of the numbers changes, but the relative ratio remains approximately the same.

The heat conductivity of the system as a whole is also important for the operation thereof. As has been indicated, there should be a heat exchanging contact between the two reactor beds. More particularly, it is of importance that there is a fixed connection, under reaction conditions, between the partition and each reactor bed. More particularly when using sintered metals as support of the catalyst bed, this can be obtained by sintering the elementary metal particles fixedly onto the wall, but it is also possible for the materials to be applied in such a manner as to have a heat transfer comparable to that of the sintered-on metals. When using a catalyst provided on the partition, optionally with a support material interposed between them, obviously one also has a good heat exchanging contact between the beds. Such systems can, for instance, consist of an assembly of (rolled-up) sheets or a monolith, in which on the walls a catalyst (optionally supported) has been provided, by means of a wash coat. In such a variant, a part of the rolled-up sheets or the monoliths, for instance an inner core, constitutes the first reactor bed, while

another part, for instance a ring around the core, constitutes the second reactor bed. Obviously, there may be more than two reactor beds. It is possible, for instance, to make a kind of shell structure with different "rings".

5   The reactor system according to the invention is applicable to each heterogeneously catalyzed gas phase reaction, but is more particularly suitable for those reactions that have a strong thermal effect, that is, highly endothermic or exothermic reactions, or reactions whose

10   selectivity is highly temperature-dependent.

In the embodiment according to the invention based on sintered metal beds, it is possible to work with a high to very high spatial throughput rate without the catalyst being blown (gaseous reactants) or washed (liquid reactants) from

15   the reactor. Nor does "channeling" occur. Because in the reactor according to the invention the catalyst particles are much better fixed, such a reactor allows working at a much higher velocity of the reactants (and consequently a much higher pressure drop across the reactor). Another

20   important advantage of fixing the catalyst bodies in the reactor according to this embodiment, is evident when dust is deposited on the catalyst bed. In reactors according to the present invention, a pulse of gas of high pressure can be sent through the reactor in a direction opposite to that

25   of the stream of reactants. This pressure pulse blows the dust off the catalyst bed; as a result, clogging can be prevented without opening the reactor, which is technically very attractive.

With non-sintered material, the reactor bed has a high

30   porosity adjacent the wall, owing to the fact that the shape of the material particles and the wall do not conform to each other. As a result, there is little catalyst present at this location and relatively much less feed will be converted. This effect is enhanced in that the high porosity

35   has low pressure losses and the feed will flow preferentially along the wall. By sintering, on the other hand, conformity with the wall is improved and the porosity

adjacent the wall is of the order of magnitude of the bed
material not located adjacent the wall. Moreover, by
applying the catalyst after filling and sintering of the
reactor, catalyst is also deposited on the wall. These two
5   effects have as a result that leakage along the wall is much
less and the reactor as a whole can be made of shorter
construction. Thus the pressure drop remains limited.

When using a reactor system based on plates or a
honeycomb, the advantage that no leakage occurs is gained to
10   a lesser extent, but on the other hand these reactors are
simpler to construct and have a lower pressure drop and are
less prone to clogging.

The invention is particularly suitable for carrying out
highly exothermic or endothermic catalytic reactions. As an
15   example of such a reaction, the oxidation of methane is
described. As an example of a reaction whose selectivity is
to a large extent determined by the temperature, the
selective oxidation of hydrogen sulfide is taken. In this
case the removal of thermal energy is of great significance
20   since above a temperature of about 300°C the oxidation of
sulfur vapor to the undesired sulfur dioxide starts to
proceed. Use of a reactor system according to the invention
makes it possible to purify gas streams of a hydrogen
sulfide content of, for instance, 10% by volume highly
25   efficiently. The hydrogen sulfide is selectively oxidized to
elementary sulfur which is extremely easy to separate
through condensation. Because such gas mixtures cannot be
properly processed in a Claus process, the invention is of
particularly great importance for this purpose.

30   As has already been indicated, the reactor system that
is used according to the invention can be made up in a
number of ways.

When using reactor beds based on sintered metal
particles, in a first variant the reactor beds are arranged
35   concentrically around each other. According to another
variant, the reactor beds are plate-shaped, one or more

first interconnected reactor beds being alternated in layers
with one or more interconnected second reactor beds.

The reactor beds based on sintered particles are most
preferably made up of more or less isotropic particles, more
5 particularly with a fairly narrow particle size
distribution. When using such elementary particles, a
catalyst system with very good properties is obtained.

The material of which the elementary particles consist
is preferably metal, but can also be alumina, silica,
10 silica-alumina, zeolite, titanium dioxide, zinc oxide or
zirconium oxide, or oxides of a combination of elements,
such as spinel ($MgAl_2O_4$), mullite ($3Al_2O_3.2SiO_2$) or
cordierite ($2MgO.2Al_2O_3.5SiO_2$), as well as carbides, nitrides
and borides of elements such as silicon, tungsten, titanium
15 and vanadium. The preference is for metal or metal alloys,
because elementary particles consisting of these materials
can be fixedly connected to each other and to the partition
wall relatively easily by sintering. The metal or the metal
alloy can then be catalytically active itself or be rendered
20 catalytically active, but it is also possible to provide a
catalytically active material thereon. One of the advantages
of a catalyst on such metal particles resides in the better
heat distribution by the use of the metal. On a microscale
it is observed that the heat conduct in the catalyst is
25 better, so that a more efficient use can be made of the
catalyst. This has an influence *inter alia* on the activity,
but can also be of importance for the selectivity, for
instance in case the selectivity is highly dependent on the
temperature, since according to the invention a much more
30 homogeneous temperature distribution is obtained in the
catalyst.

Suitable metals for use in elementary particles are
inter alia nickel, iron, chromium, manganese, vanadium,
cobalt, copper, titanium, zirconium, hafnium, tin, antimony
35 silver, gold, platinum, palladium, tungsten, tantalum, as
well as the lanthanides and actinides. The elementary
particles can consist of substantially pure metal or of an

alloy of two or more metals, which alloy can also contain non-metallic components, such as carbon, nitrogen, oxygen, sulfur, silicon, and the like.

5   According to another embodiment of the invention, the elementary particles consist of fibers or threads, preferably of a diameter of 0.5 mm at most, preferably of 1-250 μm. The materials of which these particles are manufactured preferably comprise carbon and metal or metal alloys.

10   According to another embodiment of the invention, a plate reactor is used, for instance made up of a more or less flat plate, which is provided with a corrugated plate, welded onto the flat plate along the tops of the corrugated plate. This assembly is then (for instance rolled up and)
15 welded together again, so that a reactor is obtained, consisting of a large number of channels which extend parallel to each other, on opposite sides of the plates. This reactor can be provided with a coat with catalyst in a manner similar to that described hereinabove. The ends of
20 the reactor are provided with appropriate constructions to ensure that the various reactants and reaction products are distributed over the proper channels. The metals of which such a reactor can be manufactured are generally the same metals as described hereinabove in relation to the sintered
25 metals. There is a particular preference for an alloy of *inter alia* iron and chromium, known under the name of FeCralloy[R]. The invention also relates to such a plate reactor.

     According to yet another variant of the invention, as
30 reactor system a honeycomb or monolith is used. Such systems are known and are generally characterized on the basis of the materials of which they are made and the number of channels per unit area. Monoliths can be manufactured from ceramic materials, such as mullite ($Al_6Si_2O_{13}$), titanium
35 dioxide, and α-alumina, or of metals, the above-mentioned metals being specifically eligible. Typical cell densities of monoliths are between 100 and 400 cells per (inch)^2. The

cell walls are thin and vary between 50 and 200 μm. At a cell density of 400 cpi, about 3500 m² surface per m³ monolith is available.

In a next variant of the invention, as a reactor system
5   a foam or other porous structure is used.

The reactor system according to the invention, as has already been indicated, can already be catalytically active of itself or be activated by treatment. However, it is also very well possible to provide a catalytically active
10   material on the fixedly connected elementary bodies. More particularly, it is possible first to provide a (highly) porous support on the metal surface or alloy surface and thereafter to provide the catalytically active component on the support. This last can be of significance if the
15   catalytically active component may not come into direct contact with the material of the bodies sintered together, so as to prevent undesired interactions between the material of the bodies and the catalytically active component.

When applying the catalyst, first a dispersion of a
20   support and/or the catalytically active material (or a precursor thereof) in a liquid is prepared and thereafter this liquid is suitably applied to the fixedly connected elementary bodies. This can be done, for instance, by vacuumizing the bed to which the support and/or the
25   catalytically active material are to be applied and thereafter sucking the dispersion into the bed, so that the bed is impregnated. If a support is provided first, the operation can be repeated with the catalytically active component or precursor thereof.

30   The composition of the dispersion and the conditions for manufacturing the system are preferably chosen such that the viscosity of the impregnation liquid is raised upon impregnation, since in that way it is possible to remove the liquid phase from the dispersion without the distribution of
35   the catalytically active material being substantially disturbed. Moreover, in this way a better distribution of the catalytically active material over the fixedly connected

elementary bodies is obtained. A number of methods are conceivable for increasing the viscosity of the liquid. A first method is to cool to below the solidification point thereof, so that the entire mass solidifies. By using
5 vacuum, the system can then be freeze-dried. Another possibility, and this one is preferred, is to incorporate a small amount of agar or another substance with comparable activity into the dispersion, which affords the possibility of introducing the dispersion into the system at increased
10 temperature and thereafter fixing the system by simply cooling off. Thereupon the liquid can be removed under vacuum or otherwise, and the agar can be removed at increased temperature through pyrolysis. The suitable amount of agar is substantially determined by the desire that it
15 must be possible for the liquid to become sufficiently viscous or even solid. Suitable concentrations are between 0.05 and 1.0% by weight.

It is also possible to apply the catalyst as a so-called wash coat.
20 In the drawing, the invention is further explained. Fig. 1 shows a flow diagram of a reaction in which in a first stage an exothermic reaction is carried out, while in a second stage an endothermic reaction occurs.

Fig. 2 schematically represents a reactor system based
25 on a plate reactor.

Fig. 1 shows two reactors 1, 2 which via a wall 3 are in heat exchanging contact with each other. Via line 4, reactants are supplied to reactor 1, while the reaction mixture is discharged via line 5 and is passed to the inlet
30 of reactor 2. Via line 6 the reaction mixture egressing from reactor 2 is thereupon discharged.

In Fig. 2 a schematic arrangement of a plate reactor is given. The compartments of the first reactor (1^a, 1^b, 1^c, 1^d, 1^e) are separated from the compartments of the second
35 reactor (2^a, 2^b, 2^c, 2^d) by the intervening partitions.

The invention will now be elucidated in and by a few examples, which are not intended as a limitation of the invention.

5   Example 1

A reactor consisting of a continuous porous metal structure is fixedly connected through the partition to a second reactor, likewise consisting of a continuous porous

10   metal structure, so that a heat exchanging contact is present. The porous metal structures are made up of metal particles fixedly sintered to each other and to the partition.

In the first reactor, the surface exposed to the gas

15   phase is catalytically active for the oxidation of methane. To that end, a thermostable alumina support provided with copper has been applied to the surface of the metal in the first reactor.

In the second reactor, the surface exposed to the gas

20   phase is catalytically active for the steam reforming of methane. To that end, an alumina support with nickel thereon has been applied to the metal surface of the second reactor.

Through the first reactor, a methane/air mixture is passed continuously, with a methane/air ratio (based on

25   volume) at the reactor inlet of 0.03, and with a temperature of 550°C. In the first reactor the methane reacts completely with the oxygen through the contact with the catalyst, so that the temperature in the reactor rises. The maximum value the temperature achieves is about 900°C.

30   Through the second reactor, cocurrently and continuously, a methane/steam mixture is passed with a methane/steam ratio (molar) at the reactor inlet of 0.33.

In the presence of the catalyst, methane reacts completely with steam to form CO and H_2. The temperature at

35   the inlet is 600°C, which achieves a maximum value of about 800°C.

The heat generated in the first reactor is sufficient for the endothermic reaction in the second reactor. This heat is passed to the second reactor through the conducting partition. For transferring a sufficient amount of heat to

5   the second reactor, the amount of methane that is converted in the first reactor is approximately half of the amount of methane that reacts in the second reactor.

Example 2

10

A reactor consisting of a continuous porous metal structure is fixedly connected via the partition to a second reactor, likewise consisting of a continuous porous metal structure, so that a heat exchanging contact is present. The

15   porous metal structures are made up of metal particles sintered fixedly to each other and to the partition.

In the first reactor, the surface exposed to the gas phase is catalytically active for the oxidation of methane. To that end, a thermostable alumina support provided with

20   copper has been applied to the surface of the metal in the first reactor.

In the second reactor, the surface exposed to the gas phase is catalytically active for the conversion of ethylbenzene into styrene. To that end, an iron/chromium

25   oxide catalyst on an alumina support has been applied to the metal surface of the second reactor.

Through the first reactor, a methane/air mixture is passed continuously, with a methane/air ratio (based on volume) at the reactor inlet of 0.03, and with a temperature

30   of 550°C. In the first reactor the methane reacts completely with the oxygen through the contact with the catalyst, so that the temperature in the reactor rises. The maximum value the temperature achieves is about 900°C.

Through the second reactor, cocurrently and

35   continuously, an ethylbenzene/steam mixture is passed with an ethylbenzene/steam mass ratio at the reactor inlet of 1.

In the presence of the catalyst, ethylbenzene reacts with steam to form styrene at a pressure of 0.4 bar. The temperature at the inlet is 550°C, which rises with the passage through the reactor and achieves a maximum value of
5   about 650°C. The conversion of ethylbenzene is 50%.

The unreacted ethylbenzene is separated from the reaction mixture and returned to the reactor inlet. Styrene is also separated and recovered.

The heat generated in the first reactor is sufficient
10   for the endothermic reaction in the second reactor. This heat is passed to the second reactor through the conducting partition. For transferring a sufficient amount of heat to the second reactor, the amount of methane that is converted in the first reactor is 15 mol.% of the amount of
15   ethylbenzene supplied to the second reactor.

Example 3

A reactor consisting of a continuous porous metal
20   structure is fixedly connected via the partition with a second reactor, likewise consisting of a continuous porous metal structure, so that a heat exchanging contact is present. The porous metal structures are made up of metal particles fixedly sintered to each other and to the
25   partition.

In the first reactor, the surface exposed to the gas phase is catalytically active for the oxidation of methanol. To that end, an iron/molybdenum oxide catalyst on alumina has been applied to the surface of the metal in the first
30   reactor.

In the second reactor, the surface exposed to the gas phase is catalytically active for the conversion of methanol into synthesis gas. To that end, a copper/zinc catalyst on alumina has been applied to the metal surface of the second
35   reactor.

Through the first reactor, a methanol/air mixture is passed continuously with a methane/air ratio (based on

volume) at the reactor inlet of 0.06 and a temperature of about 300°C. In the first reactor the methanol reacts in the presence of the catalyst with oxygen. As a result, the temperature rises and achieves a maximum value of about

5   400°C. The conversion of methanol into formaldehyde is 95%.

Through the second reactor, cocurrently and continuously, a methanol/steam mixture is passed with a methanol/steam ratio (molar) at the reactor inlet of 0.8.

In the presence of the catalyst, methanol reacts with

10   steam to form CO and H_2. The temperature at the inlet is 200°C. With the passage through the reactor, it rises and achieves a maximum value of about 250°C. The conversion of methanol is 100%.

The heat generated in the first reactor is sufficient

15   for the endothermic reaction in the second reactor. This heat is passed to the second reactor through the conducting partition. For transferring a sufficient amount of heat to the second reactor, the amount of methanol that is supplied to the first reactor is about 60% of the amount of methanol

20   that reacts in the second reactor.

CLAIMS

1.   A method for carrying out two chemical reactions in a
reactor system comprising at least two mutually separate
reactor beds, of which the surfaces exposed to the reactants
are catalytically active for the chemical reactions
5   concerned, and at least one partition, wherein
  -   at least one first reactor bed is present, which is
      bounded by at least one partition, which bed is based on
      a continuous porous structure and which bed is fixedly
      connected to said partition,
10 -   at least one second bed is present, which is based on a
      continuous porous structure, and which bed is fixedly
      connected to said partition, and
  -   said second bed, with respect to the first bed, is
      disposed on the other side of said partition, so that a
15   heat exchanging contact between said beds is present and
      the reaction heat of a first chemical reaction which is
      carried out in said first reactor bed is supplied or
      absorbed by carrying out a second chemical reaction in
      said second bed.

20 2.   A method according to claim 1, wherein two or more
    first reactor beds and/or two or more second reactor beds
    and a corresponding number of partitions are used.

    3.   A method according to claim 1 or 2, wherein the porous
    structure of at least one of said reactor beds consists of a
25 porous metal.

    4.   A method according to claim 3, wherein both beds
    consist of porous metal.

    5.   A method according to claim 3 or 4, wherein as porous
    metal, sintered metal particles, sintered metal fibers or
30 metal foam is used.

    6.   A method according to claim 1 or 2, wherein the reactor
    beds are formed by a monolith structure of which a part of
    the channels is used as first reactor bed and a part of the
    channels is used as second reactor bed.

7. A method according to claim 1 or 2, wherein each of the reactor beds is formed by a monolith structure.

8. A method according to claim 1 or 2, wherein the reactor beds are formed by the channels of an assembly of at least two metal plates, wherein to a first plate at least one corrugated second plate is attached, so that in the longitudinal direction channels are formed between the tops of the corrugated plate and the two surfaces of said first plate.

9. A method according to claim 8, wherein said assembly is rolled up.

10. A method according to claims 1-9, wherein in the first reactor bed an endothermic reaction is carried out and in the second reactor bed an exothermic reaction is carried out.

11. A method according to claims 1-9, wherein in the first reactor bed an exothermic reaction is carried out and in the second reactor bed an endothermic reaction is carried out.

12. A method according to claims 1-11, wherein a multi-stage reaction is carried out, wherein at least one stage of this reaction has a positive and at least one stage has a negative heat effect, and wherein said stages are carried out in said first and second reactor bed.

13 A reactor suitable for carrying out the method according to claim 8 or 9, comprising two reactor beds which are formed by the channels of an assembly of two metal plates, while to a first plate a corrugated second plate is attached, so that in the longitudinal direction channels are formed between the tops of the corrugated plate and the two surfaces of said first plate.

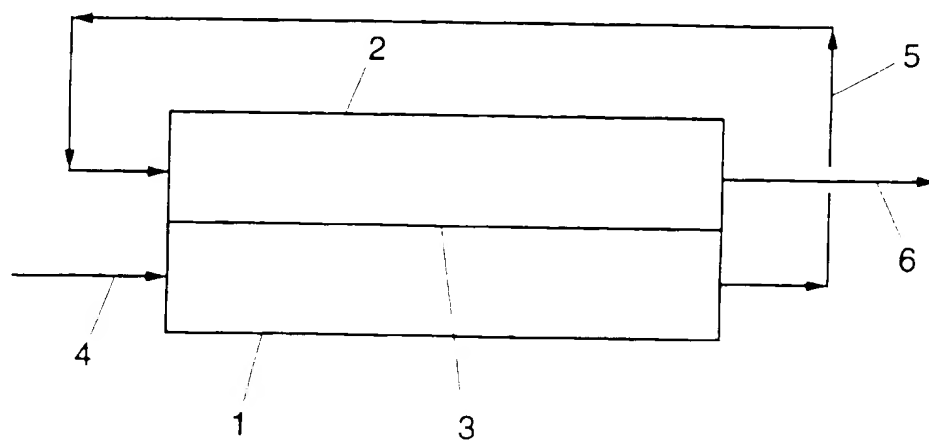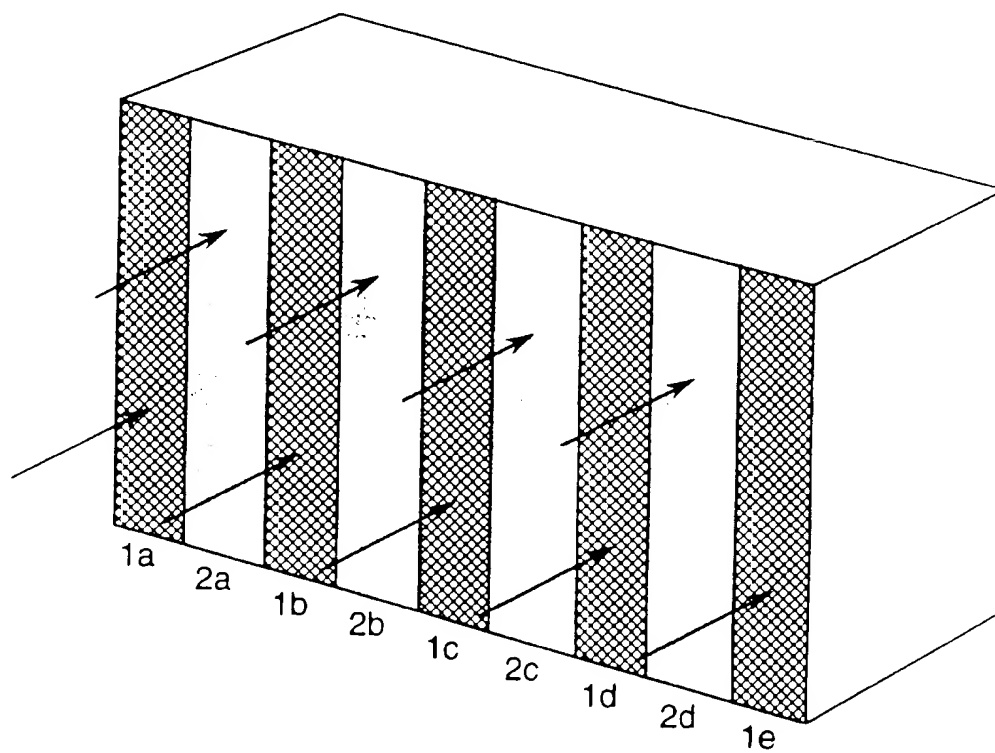14. A reactor according to claim 13, wherein said assembly is rolled up.

FIG. 1

FIG. 2

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   B01J8/02   B01J8/04   B01J12/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6   B01J   H01M   C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	FR,A,1 603 801 (LA SOCIÉTÉ CHIMIQUE DE LA GRANDE PAROISSE, AZOTE ET PRODUITS CHIMIQUES) 7 June 1971 see page 1, line 1 - line 3 see page 1, line 33 - page 2, line 10 see page 2, line 38 - line 35 see figure	1-4, 10-12
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[X] Further documents are listed in the continuation of box C

[X] Patent family members are listed in annex

* Special categories of cited documents :

'A' document defining the general state of the art which is not considered to be of particular relevance

'E' earlier document but published on or after the international filing date

'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

'O' document referring to an oral disclosure, use, exhibition or other means

'P' document published prior to the international filing date but later than the priority date claimed

'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

'&' document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 July 1996	1 2 -07- 1996

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel (+31-70) 340-2040, Tx. 31 651 epo nl. Fax (+31-70) 340-3016	Stevnsborg, N

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
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US-A-3925252	09-12-75	NONE		